Expedient Syntheses of Neutral and Cationic Au(I)-NHC Complexes

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Dedicated to the memory of Professor István E. Markó

ABSTRACT: The synthesis and isolation of gold(I) pre-catalysts often requires the generation of several isolable intermediates as well as numerous purification steps. New protocols for the expedient synthesis of neutral [Au(OH)(NHC)] and [Au(CH_2COCH_3)(NHC)] species from [AuCl(NHC)] or [AuCl(DMS)] precursors bearing a variety of *N*-heterocyclic carbene (NHC) ligands are presented. These methods can be employed in a telescoping manner for the synthesis of catalytically relevant [Au(NTf_2)(NHC)] and [Au(NHC)($NCCH_3$)][BF_4] complexes. These attractive methods are straightforward and practical leading to various complexes in high isolated yields and purity.

INTRODUCTION

The field of gold chemistry and catalysis continues to flourish after a decade of important advances.[1] The exploration of gold(I)-NHC chemistry in particular has gained increased attention mainly due to the ever-growing development of NHC (NHC = N-heterocyclic carbene) ligand design and tunability (Figure 1).[2] Our synthetic studies of Au-NHC complexes initially targeted the isolation of [AuCl(NHC)] (**1**) via the reaction of [AuCl(DMS)] (DMS = dimethylsulfide) with the free NHC.[2b] This and following simpler synthetic protocols have rendered gold(I) complexes such as **1** excellent precursors for a variety of neutral and cationic gold(I) species (Figure 2).[3] Active gold catalysts are generally prepared by anion metathesis through the addition of a silver(I) salt AgX (X = OTf, NTf_2, BF_4, PF_6 or SbF_6) to these gold(I) chloride precursors (Figure 2, route IA).[3] Using this strategy, [Au(NHC)($NCCH_3$)][X] (X = BF_4, PF_6)[4] and [Au(NTf_2)(NHC)][5] complexes have readily been accessed.

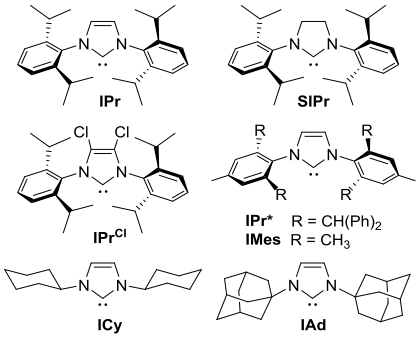


Figure 1. Selected NHCs used in this work.

Problematically, silver salts were shown to persist as impurities and interfere with catalytic reactions through the formation of silver-stabilized intermediates (*e.g. gem*-dimetallated complexes)[6] or catalytically active acids.[7] Furthermore, avoiding the use of light- and moisture sensitive silver salts is highly desirable in an effort to decrease cost and to simplify handling.[8] In this context, gold hydroxide complexes, [Au(OH)(NHC)] (**2**), have been developed (Figure 2, route IB);[9] these complexes can be activated by Brønsted acids (*e.g.* HOTf, $HNTf_2$, $HBF_4{\cdot}OEt_2$, H_3OPF_6 , $2HF{\cdot}SbF_5$ or $NEt_3{\cdot}3HF$[10]) and mineral acids (HNO_3, H_2SO_4 or H_3PO_4)[11] instead of silver salts to deliver the same catalytically active cationic species (Figure 2, route IC). These formal acid-base reactions are facilitated by the high Brønsted basicity of the hydroxide precursors.[12]

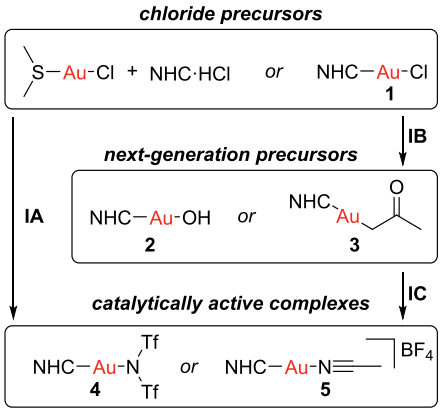


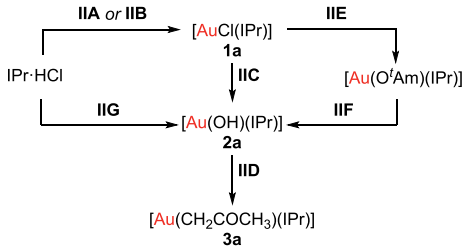
Figure 2. General synthetic analysis for the formation of gold(I)-NHC complexes: **IA** silver-based, **IB** silver-free and **IC** acid-based transformations.

Even though numerous catalytic methodologies have successfully employed this mode of activation *in situ*,[13] the use of pre-formed catalysts is still desirable to avoid issues with acid-sensitive reactions, substrates and parasitic or undesired

silver-mediated reactions. Consequently, these silver-free protocols have allowed the isolation of key precursors such as [Au(NTf$_2$)(IPr)] (**4a**)[5] and [Au(IPr)(NCCH$_3$)][BF$_4$] (**5a**)[14] starting from [Au(OH)(IPr)] (**2a**) (Figure 2, route IC). Recently, the newly reported neutral gold(I)-acetonyl complex, [Au(CH$_2$COCH$_3$)(IPr)] (**3a**), has displayed similar interesting reactivity.[15] Release of acetone upon reaction of gold-acetonyl complexes with acids resulted in a range of gold complexes, including **4a** (Figure 2, route IC)[15] and [Au(OTf)(IPr)].[16]

An evaluation of the previously-reported procedures for syntheses of [AuCl(NHC)] (**1**) and [Au(OH)(NHC)] (**2**) indicates that gold(I)-NHC species are compatible with various bases (Scheme 1). The first synthesis of [AuCl(IPr)] (**1a**) consisted of generating the free carbene by reacting IPr·HCl[17] with KO^{t}Bu[18] followed by the addition of [AuCl(DMS)] (Scheme 1, route IIA).[2b] This has now been improved upon, using a straightforward one-pot system with potassium carbonate as base; the reaction proceeds *via* the *in situ* formation of "*ate*" complexes, [NHC·H][AuCl$_2$] (Scheme 1, routes IIB and IIC).[19] Crucially, use of an excess of base and prolonged reaction times in the latter procedure leads to [Au(CH$_2$COCH$_3$)(IPr)] (**3a**) instead of **1a**.[15] Alternatively, this gold(I)-acetonyl complex can be formed from [Au(OH)(IPr)] (**2a**) in the absence of an external base by simply stirring it in acetone (Scheme 1, route IID).[15]

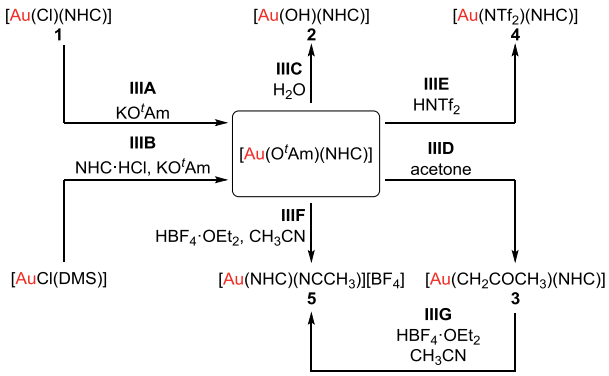
Scheme 1. Synthetic access to [AuCl(IPr)] (1a) and [Au(OH)(IPr)] (2a)[a]



[a]Procedures: **IIA**: 1) KO^{t}Bu (1.1 equiv.), THF, argon, rt 2) [AuCl(DMS)], THF, argon, rt;[2d] **IIB**: [AuCl(DMS)], K$_2$CO$_3$ (1 equiv.), acetone, in air, 60 °C;[19] **IIC**: 1) NaOH (6 equiv.), ^{t}AmOH (0.2 equiv.), THF, in air, rt, 2) H$_2$O, in air, rt.[20] **IID**: acetone, rt;[15] **IIE**: KO^{t}Am (1.3 equiv.), C$_6$H$_6$, argon, rt;[20] **IIF**: H$_2$O, in air, rt;[20] **IIG**: 1) [AuCl(DMS)], KO^{t}Bu (1.5 equiv.), THF 2) KO^{t}Bu (3 equiv.), toluene 3) filtration, H$_2$O, in air, rt.[20]

The formation of [Au(OH)(IPr)] (**2a**) from [AuCl(IPr)] (**1a**) was initially performed using alkali earth hydroxide bases at slightly elevated temperatures;[9a,9c,21] however, an improved procedure using a mixture of NaOH and *tert*-amyl alcohol was later reported (Scheme 1, route IIC).[20] This latter route was demonstrated to proceed through formation of [Au(O^{t}Am)(IPr)] and the overall transformation could be carried out sequentially by first reacting **1a** with a toluene solution of potassium *tert*-amylate followed by the addition of water (Scheme 1, route IIE-IIF). Furthermore, the viability of a one-pot sequential approach starting from IPr·HCl was also demonstrated (Scheme 1, route IIG). Although route **IIC** is one of the best procedures to form **2**, it still requires long reaction times (24 h). Examining these reports, we noticed that the use of a toluene solution of the alkoxide base, to form species **2** starting from **1** (Scheme 1, route IIE-IIF), avoids problems associated with the use of hygroscopic hydroxide salts (*e.g.*, KOH, CsOH) while significantly accelerating reactions. In the context, we aim herein to extend this procedure to other NHC ligands (Scheme 2, route IIIA-IIIC). Another objective of the present study was to synthesize species **2** directly from [AuCl(DMS)] and NHC·HCl (Scheme 2, route IIIB-IIIC). The high reactivity of [Au(O^{t}Am)(IPr)] (as apparent from its rapid hydrolysis in air) prompted us to further investigate the feasibility of quenching this Au-OR moiety with various acidic partners, such as acetone, trifluoromethanesulfonimide acid or tetrafluoroboric acid to form complexes **3**-**5**, respectively, in a sequential manner (Scheme 2, routes IIID, IIIE and IIIF). In addition, we herein expand the utility of [Au(CH$_2$COCH$_3$)(NHC)] (**3**) as silver-free synthons for the formation of a range of new [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**) *via* reactions with tetrafluoroboric acid diethyl ether complex (Scheme 2, route IIIG).

Scheme 2. Targeted sequential formation of complexes 2-5



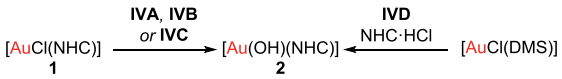
RESULTS AND DISCUSSION

Synthesis of [Au(OH)(NHC)]. We began by adapting the previously described syntheses of [Au(OH)(IPr)] (**2a**) from [AuCl(IPr)] (**1a**) (Scheme 1, route IIE-IIF) to a procedure that could be performed in air using technical grade toluene and a toluene solution of potassium *tert*-amylate (commercially available) as base (Table 1, route IVC).[22] Gratifyingly, reactions reached completion within one hour and **2a-d** could be isolated in similar or improved yields as compared to the previously reported procedure that involved overnight reactions (Table 1, entries 1-4, routes IVA *versus* IVC). Due to its low solubility in toluene, the reaction of the complex bearing the IPr* ligand did not reach completion in one hour initially, but complete conversion was obtained by using a mixture of toluene and THF (1:1). As expected from the precedent study,[20] the gold hydroxides complexes bearing IMes, ICy or IAd could not be cleanly isolated (in air) (Table 1, entries 5-7, routes IVA and IVC).

A change of solvent to a 1:1 toluene/THF mixture allowed the sequential formation of [Au(OH)(NHC)] (**2**) directly from [AuCl(DMS)] and NHC·HCl, but not selectively and in reduced yields (Table 1, route IVD). Products bearing ligands IPr, SIPr and IPr^{Cl} consistently contained a small amount of the corresponding [Au(NHC)$_2$][Cl] side-product. These bis-ligated complexes are known to form upon reaction of the imidazolium salt with the *in situ* formed [AuCl(IPr)] (**1**) (assisted by base)[23] or with [Au(OH)(NHC)] (**2**).[24] The absence of this side-product in the reaction involving the IPr* ligand was attributed to NHC increased steric bulk.[25] Interestingly, when the reaction of [AuCl(DMS)] and IPr*·HCl was performed under these conditions but using THF as sole solvent, [AuCl(IPr*)] (**1c**) rather than

[Au(OH)(IPr*)] (**2c**) was obtained exclusively in 73% yield, providing an alternative synthesis to the previously reported method.[19]

Table 1. Synthesis of [Au(OH)(NHC)] (2)[a]

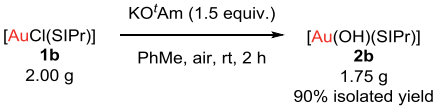


	Complex (NHC)	IVA[20]	IVB[21]	IVC	IVD
1	**2a** (IPr)	87	-	92	(79)[b]
2	**2b** (SIPr)	72	-	71	(51)[c]
3	**2c** (IPr^{Cl})	76	-	79	(31)[d]
4	**2d** (IPr*)	75	-	86[e]	77
5	**2e** (IMes)	0	98	0	-
6	**2f** (ICy)	0	93	0	-
7	**2g** (IAd)	0	80	0	-

[a]Isolated yields (%) of syntheses on a 0.3 mmol scale are given. Procedures: **IVA** NaOH (6 equiv.), ^{t}AmOH (0.2 equiv.), THF, in air, rt; **IVB** CsOH (10 equiv.), C_6H_6, argon, rt;[21] **IVC** 1) KO^{t}Am (1.5 equiv), toluene 2) H_2O, in air, rt; **IVD** 1) KO^{t}Am (1.5 equiv), toluene/THF (1:1) 2) H_2O, in air, rt. [b]Mixture with $[Au(IPr)_2][Cl]$ (5%). [d]Mixture with $[Au(SIPr)_2][Cl]$ (16%). [d]Mixture with $[Au(IPr^{Cl})_2][Cl]$ (35%). [e]toluene/THF (1:1).

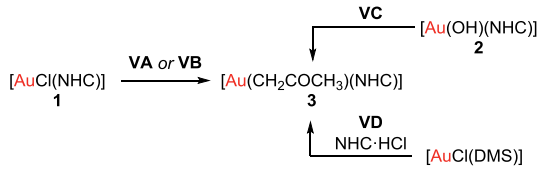
The practical value of a new methodology is best evaluated by testing its scalability. The most recent procedure for the formation of [Au(OH)(NHC)] (**2**) from the corresponding [AuCl(NHC)] (**1**) (Table 1, route IVA) was demonstrated to be scalable up to multi-gram quantities.[20,26] We were delighted to obtain a very good yield of 90% when we conducted a large scale synthesis of [Au(OH)(SIPr)] (**2b**) (Scheme 3). It should be noted that, although the yield is similar to the one obtained with the previously reported procedure,[20] the reaction time can be dramatically shortened (2 h compared to 24 h).

Scheme 3. Large scale synthesis of [Au(OH)(SIPr)] (2b)



Synthesis of [Au(CH$_2$COCH$_3$)(NHC)]. We continued our exploration by evaluating the direct synthesis of [Au(CH$_2$COCH$_3$)(NHC)] (**3**) from [AuCl(NHC)] (**1**) or [AuCl(DMS)] and NHC·HCl using KO^{t}Am in toluene as base (Table 2, routes VB and VD). These transformations could be performed using acetone and a mixture of acetone and toluene (1:1) as solvents, respectively. The synthesis from [AuCl(NHC)] (**1**) gave lower yields than the previously reported procedure for complexes bearing IPr, SIPr or IPr^{Cl} (Table 2, entries 1-3, route VB *versus* route VA). Moreover, significant amounts of side-product were formed in reactions with the IPr or SIPr ligands. These were assigned to the corresponding carbon-bound complexes of the self-condensation product of acetone, [Au(CH$_2$COC(H)C(CH$_3$)$_2$)(NHC)] (**3'**) (Scheme 4).

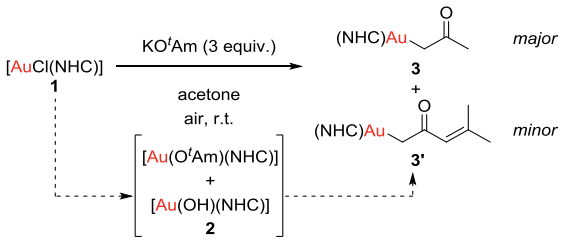
Table 2. Synthesis of [Au(CH$_2$COCH$_3$)(NHC)] (3)[a]



Entry	Complex (NHC)	VA	VB	VC	VD
1	**3a** (IPr)	80[15]	46[b]	82[15]	51
2	**3b** (SIPr)	97[15]	41[c]	-	54
3	**3c** (IPr^{Cl})	92[15]	56	-	56
4	**3d** (IPr*)	81[15]	71[d]	-	74
5	**3e** (IMes)	71[15]	0	-	(>99)[e]
6	**3f** (ICy)	-	0	-	0
7	**3g** (IAd)	65[15]	(>99)[e]	-	71

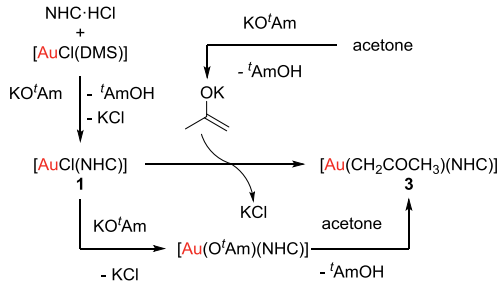
[a]Isolated yields (%) of syntheses on a 0.3 mmol scale are given. Procedures: **VA** K_2CO_3 (6 equiv.), acetone, in air, 60 °C;[15] **VB** KO^{t}Am (3 equiv.), acetone, in air, rt; **VC** acetone, rt;[15] **VD** KO^{t}Am (3 equiv.), acetone/toluene, in air, rt. [b]Mixture with [Au(CH$_2$COC(H)C(CH$_3$)$_2$)(IPr)] (**3a'**, 28%). [c]Mixture with [Au(CH$_2$COC(H)C(CH$_3$)$_2$)(SIPr)] (**3b'**, 16%). [d]Acetone/THF (1:1), mixture with **2d** (18%). [e]Conversion of **1** to **3**, determined by ^{1}H-NMR.

Scheme 4. Hypothetical formation of Au(I)-NHC-ketonyl products 3 and 3'



We found **3'** to be equally susceptible to protonolysis as the corresponding [Au(CH$_2$COCH$_3$)(NHC)] (**3**), and the mixtures could be used in subsequent transformations towards [Au(NTf$_2$)(NHC)] (**4**) and [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**) without affecting the overall outcome of the reactions (see Table 4). Unexpectedly, when we tested the formation of [Au(CH$_2$COCH$_3$)(IPr*)] (**3d**) from [AuCl(IPr*)] (**1d**), we obtained a mixture of the desired product and [Au(OH)(IPr*)] (**2d**). This result can be explained either by slower reaction of **2d** with acetone to form **3d** because of the sheer bulk of the IPr* ligand,[25] or the operation of two different mechanisms. This mixture could be used in subsequent synthetic steps (towards **4d** and **5d**) without affecting the overall outcome. Alternatively, adding THF to the reaction mixture restored full conversion to **3d** in one hour (Table 2, route VB, entry 4). Similar to the previous synthesis of [Au(OH)(NHC)] (**2**), decomposition occurred for complexes bearing IMes or ICy ligands (Table 2, route VB, entries 5-6). In contrast, the reaction of [AuCl(IAd)] (**1g**) gave complete conversion to [Au(CH$_2$COCH$_3$)(IAd)] (**3g**); however, several purification attempts were insufficient to remove unidentified minor impurities (Table 2, route VB, entry 7).

Scheme 5. Routes to [Au(CH$_2$COCH$_3$)(NHC)] (3)

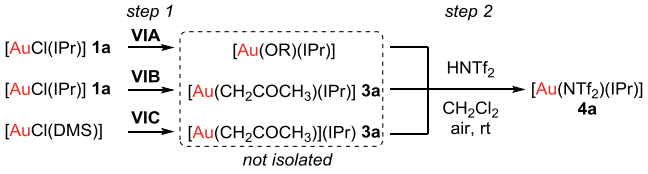


The sequential synthesis of [Au(CH$_2$COCH$_3$)(NHC)] (**3**) directly from [AuCl(DMS)] and NHC·HCl were performed using a mixture of acetone and toluene (1:1) using 3 equivalents of KO^{t}Am in toluene (Table 2, route VD).[27] This amount of base was selected based on various sequential routes available (Scheme 5). [AuCl(NHC)] (**1**) would form first from reaction of the starting materials with the first equivalent of base.[19] The second equivalent of base would then form [Au(O^{t}Am)(IPr)] that would react with acetone to produce **3**. Alternatively, the base was hypothesized to activate acetone to its potassium enolate form, directly substituting the chloride of **1** with the acetonyl fragment.

This method proved successful for all ligands tested, except for IMes and ICy (Table 2, route VD, entries 1-7); **3e** was obtained with impurities and, in the case of **3f**, decomposition occurred (Table 2, route VD, entries 6-7). The disadvantage of reduced yields compared to the previously reported procedure (Table 2, route VA) might be outweighed by the significantly reduced reaction times from multiple days to as short as one hour in some cases.

Sequential synthesis of [Au(NTf$_2$)(IPr)]. Having established that [Au(OH)(IPr)] (**2a**) and [Au(CH$_2$COCH$_3$)(IPr)] (**3a**) are accessible from [AuCl(IPr)] (**1a**) or [AuCl(DMS)] and IPr·HCl (Tables 1 and 2, entries 1), we began evaluating the different sequential two-step and three-step transformations to access [Au(NTf$_2$)(IPr)] (**4a**) (Table 3).

Table 3. Sequential synthesis of [Au(NTf$_2$)(IPr)] (4a)[a]



Entry	Route	Solvent	Yield **4a** (%)
1	**VIA**	toluene	93
2	**VIB**	acetone	87
3	**VIC**	acetone/toluene	93

[a]R = O^{t}Am, H. Reaction conditions: 1) **VIA** KO^{t}Am (1.5 equiv.), rt; **VIB** KO^{t}Am (1.5 equiv.), rt; **VIC** NHC·HCl (1.0 equiv.), KO^{t}Am (3.0 equiv.), rt 2) HNTf$_2$, CH$_2$Cl$_2$, in air, rt.

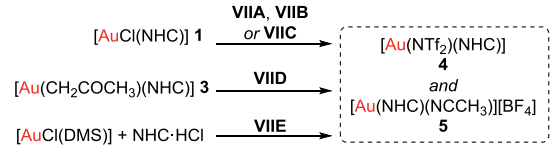
Solvent was removed from the filtrate after the first reaction step and the crude material was subsequently used without further purification. Starting from **1a**, **4a** was obtained in high yields irrespective of the choice of solvent and the resulting non-isolated intermediate formed in the first reaction step (Table 3, entries 1 and 2). Beneficially, the second reaction step could be performed in dichloromethane instead of the previously used benzene.[15,21] To avoid the previously observed [Au(IPr)$_2$][Cl] side-product in the reaction of [AuCl(DMS)] and IPr·HCl with KO^{t}Am (Table 1, route IVD, entry 1), the sequential reaction was performed with acetone in the first reaction step to ensure the formation of **3a** as intermediate. In this manner, **4a** was obtained as the sole product (Table 3, entry 3). The significantly higher isolated yields of **4a** (Table 3, entries 2-3) compared to that of **3a** (Table 2, route VB and VD, entry 1) suggested that part of the latter intermediate was lost during the purification procedure and that a sequential transformation is preferred.

Syntheses of [Au(NTf$_2$)(NHC)] and [Au(NHC)(NCCH$_3$)][BF$_4$]. The efficacy of various protocols for the synthesis of cationic [Au(NTf$_2$)(NHC)] (**4**) and [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**) bearing a variety of NHC ligands was assessed next (Table 4). Reported yields of silver-based single-step (Table 4, route VIIA) and silver-free two-step (Table 4, route VIIB) transformations starting from [AuCl(NHC)] (**1**) were compared to the single-step transformations using [Au(CH$_2$COCH$_3$)(NHC)] (**3**) (Table 4, route VIIC) and to the two-step transformations starting either from [AuCl(NHC)] (**1**) (Table 4, route VIID) or from [AuCl(DMS)] and NHC·HCl (Table 4, route VIIE).[28]

[Au(NTf$_2$)(NHC)] (**4a-e**,**g**) could be directly synthesized from [Au(CH$_2$COCH$_3$)(NHC)] (**3a-e**,**g**) in similar or higher yields compared to previous procedures (Table 4, routes VIIA, VIIB vs VIID, entries 1-6). The sequential procedure permitted synthesis of [Au(NTf$_2$)(NHC)] (**4a-d**) from [AuCl(NHC)] (**1a-d**) in generally slightly reduced yields (Table 4, route VIIC, entries 1-4). For complexes bearing IMes and IAd ligands, a pathway proceeding *via* [Au(CH$_2$COCH$_3$)(IMes)] (**3e**) and [Au(CH$_2$COCH$_3$)(IAd)] (**3g**) instead of [Au(NHC)(OR)] (R = H, ^{t}Am) was preferred, due to the sensitivity of the [Au(OH)(IMes)] (**2e**) and [Au(OH)(IAd)] (**2g**) intermediates that are formed in the sequential reactions according to route VIIC. In this context, a different sequential transformation was tested starting from [AuCl(DMS)] and NHC·HCl (Table 4, route VIIE). [Au(NTf$_2$)(IMes)] (**4e**) was obtained as the main product, although we were unable to isolate it from a small amount of unidentified side-product (Table 4, route VIIE, entry 5). Gratifyingly, [Au(NTf$_2$)(IAd)] (**4g**) was isolated in good yield and purity (Table 4, route VIIE, entry 6).

Considering [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**), only the synthesis of the congener bearing an IPr ligand (**5a**)[14] has been previously reported. Complexes bearing SIPr (**5b**)[29] or IPr^{Cl} (**5c**)[29] ligands have been used as catalysts but their syntheses have not been disclosed and complexes bearing IPr* (**5d**) and IAd (**5g**) ligands are yet to be reported. [Au(IPr)(NCCH$_3$)][BF$_4$] (**5a**) has been described to decompose to [Au(NCCH$_3$)$_4$][BF$_4$] when synthesized from [AuCl(IPr)] (**1a**) and AgBF$_4$ (Table 4, route VIIA, entry 7).[4] The successful silver-free synthesis starting from [Au(OH)(IPr)] (**2a**) (Table 4, route VIIB, entry 7) encouraged us to test the applicability of our new methods. Gratifyingly, we were able to prepare **5** in an analogous fashion to [Au(NTf$_2$)(NHC)] (**4**) starting from [Au(CH$_2$COCH$_3$)(NHC)] (**3**), simply by switching from bis(trifluoromethanesulfonyl)amine to tetrafluoroboric acid and from dichloromethane to acetonitrile (to provide the auxiliary ligand). With these modifications, [Au(NHC)(NCCH$_3$)][BF$_4$] (**5a-d**,**g**) could be isolated in good to excellent yields (Table 4, route VIID, entries 7-11).

Table 4. Syntheses of [Au(NTf$_2$)(NHC)] (4) and [Au(NHC)(NCCH$_3$)][BF$_4$] (5)[a]



Entry	Complex (NHC)	VIIA	VIIB	VIIC	VIID	VIIE
		4 (X = NTf$_2$)[b]				
1	**4a** (IPr)	69[5]	84[21]	93[d]	92	-
2	**4b** (SIPr)	73[5]	71[21]	93	97	-
3	**4c** (IPr^{Cl})	87[30]	62[21]	90	97	-
4	**4d** (IPr*)	93[25]	73[21]	86	91	-
5	**4e** (IMes)	86[5]	-	-	95	n.d.[e]
6	**4g** (IAd)	75[5]	-	-	79	80
		5 (X = BF$_4$)[c]				
7	**5a** (IPr)	-	96[f]	99	91	-
8	**5b** (SIPr)	-	-	94	97	-
9	**5c** (IPr^{Cl})	-	-	99	97	-
10	**5d** (IPr*)	-	-	78	91	-
11	**5g** (IAd)	-	-	-	84	n.d[e]

[a]Isolated yields (%) are given. Procedures (those for **5** are indicated with a prime in the experimental section): **VIIA** AgX, CH_2Cl_2, in air, rt; **VIIB** 1) KOH, THF, 30 °C 2) HX, C_6H_6, rt, in air; **VIIC** 1) KO^{t}Am (1.5 equiv.), toluene 2) HX, solvent, in air, rt; **VIID** HX, solvent, in air, rt; **VIIE** 1) KO^{t}Am (3.0 equiv.), acetone/toluene 2) HX, solvent, in air, rt. [b]Solvent = CH_2Cl_2 in procedures **VIIC** and **VIID**. [c]Solvent = CH_2Cl_2 in procedure **VIIA** (with stoichiometric CH_3CN) and CH_3CN in procedures **VIIC** and **VIID**, HBF_4·OEt was used. [d]Identical to Table 3, entry 1. [e]n.d = not determined: product could not be isolated from mixture with unidentified side-products. [f]Yield from **2a** is given.[14]

The two step sequential route from [AuCl(NHC)] (**2**) *via* [Au(OH)(NHC)] (**3**) was then applied to the synthesis of [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**). Complexes **5a-d** were obtained in good to excellent yields (Table 4, route VIIC, entries 7-10). Again, a sequential route starting from [AuCl(DMS)] and IAd·HCl that would proceed through [Au(CH$_2$COCH$_3$)(IAd)] (**3g**) was preferred for the synthesis of [Au(IAd)(NCCH$_3$)][BF$_4$] (**5g**). While the expected product formed predominantly in this reaction, a small amount of an unidentified product also formed. Attempts to purify this mixture resulted in decomposition (Table 4, route VIIE, entry 11).

Table 5. Chemical shifts in [Au(NHC)(NCCH$_3$)][BF$_4$] (5)[a]

Entry	Complex (NHC)	C^2 δ(^{13}C) (ppm)	CN δ(^{13}C) (ppm)	CH$_3$ δ(^{13}C) (ppm)	CH$_3$ δ(^{1}H) (ppm)
1	**5a** (IPr)	166.3	121.0	2.7	2.39
2	**5b** (SIPr)	188.3	121.1	2.7	2.33
3	**5c** (IPr^{Cl})	166.4	121.8	2.9	2.27
4	**5d** (IPr*)	166.7	120.8	2.9	2.62
5	**5g** (IAd)	156.9	121.9	3.2	2.31

[a]Values measures in $CDCl_3$ are given.

Spectroscopic Data of [Au(NHC)(NCCH$_3$)][BF$_4$]. Having in hand a series of [Au(NHC)(NCCH$_3$)][BF$_4$], the influence of the different NHC ligands on the [Au(NCCH$_3$)]$^+$ fragment was investigated (Table 5). ^{13}C chemical shifts of the C^2 carbene in NHCs (C^2-δ(^{13}C)), are indicative of the environment around [Au(NHC)] fragments and are thus used to gauge the Lewis acidity of gold complexes.[31,32] A downfield shift C^2-δ(^{13}C) of 166.3 ppm in [Au(IPr)(NCCH$_3$)][BF$_4$] (**5a**) relative to 159.0 ppm in [Au(IPr)][BF$_4$][33] is indicative of a less electron-deficient gold center in the former, as expected from coordination of the second ligand (NCCH$_3$).[14,34] Net electron transfer from the coordinated acetonitrile to the gold center was also apparent from downfield shifts (caused by lower shielding) of the ^{1}H and ^{13}C resonances relative to non-coordinated acetonitrile: CN-δ(^{13}C) = 116.9,[35] CH$_3$-δ(^{13}C) = 1.9 and CH$_3$-δ(^{1}H) = 2.10.[36]

Changes to the electronic configuration of the acetonitrile fragment in **5** were next probed by comparing the C≡N stretching frequencies from infrared spectra to those in non-coordinated acetonitrile. The σ-donor lone pair on the N atom of acetonitrile is weakly antibonding, and upon complexation, electron donation from the lone pair to the gold center would be expected to remove weakly antibonding electrons from the CN bond, thereby strengthening it and increasing $\nu_{C\equiv N}$.[37] Indeed, blue-shifted values of $\nu_{C\equiv N}$ were measured for **5a-d** (Table 6) relative to non-coordinated acetonitrile ($\nu_{C\equiv N}$ = 2254, 2293 cm^{-1}, doublet).[38] Unfortunately, the poor resolution and small range of $\nu_{C\equiv N}$ prohibits meaningful comparison to known metrics of π-accepting potential of ligands.[39]

Table 6. IR features of [Au(NHC)(NCCH$_3$)][BF$_4$] (5)

Entry	Complex (NHC)	$\nu_{C\equiv N}$ (cm^{-1})[a]
1	**5a** (IPr)	2359-2310
2	**5b** (SIPr)	2359-2303
3	**5c** (IPr^{Cl})	2359-2309
4	**5d** (IPr*)	2357-2308

[a]Values of neat complexes, measured by FTIR-ATR are given. Overlap and low intensity of these bands prohibited accurate determination of single values.

X-ray Structure Determination of [Au(NHC)(NCCH$_3$)][BF$_4$]. To unambiguously establish the solid state structure of the new [Au(NHC)(NCCH$_3$)][BF$_4$], crystals suitable for X-ray diffraction analyses were grown from slow diffusion of pentane into solutions of [Au(SIPr)(NCCH$_3$)][BF$_4$] (**5b**) and [Au(IPr^{Cl})(NCCH$_3$)][BF$_4$] (**5c**) in ethyl acetate and a solution of [Au(IPr*)(NCCH$_3$)][BF$_4$] (**5d**) in acetone (Figure 3). The results of diffraction studies performed on the obtained single crystals agreed with the structures determined by NMR and the coordination of acetonitrile to the gold center was confirmed. Bond angles C-Au-N indicated near-linear structures and bond lengths C-Au and Au-N showed little variation (Table 7). As previously observed for the PF$_6$-based analogous compound [Au(IPr)(NCCH$_3$)][PF$_6$],[4] the N≡C bonds in the coordinated acetonitrile molecules were slightly shorter than in non-coordinated acetonitrile (1.141 Å),[40] consistent with the measured increases in stretching frequencies (Table 6).

5b **5c** **5d**

Figure 3. Thermal ellipsoid representations of [Au(NHC)(NCCH$_3$)][BF$_4$] (**5b-d**) at 50% probability. Most hydrogen atoms and a molecule of ethyl acetate has been omitted from **5c**, for clarity. Selected bond lengths C1-Au1, Au1-N30, C30-N30, C72-N71 (Å) and angles C1-Au1-N30 and C1-Au1-N71 (°) are given in Table 7.

Table 7. Bond angles and lengths in 5b-d.

Entry	Complex (NHC)	C-Au-N (°)	C-Au (Å)	Au-N (Å)	N≡C (Å)
1	**5b** (SIPr)	178.54(13)	1.981(3)	2.005(3)	1.132(5)
2[a]	**5c** (IPr^{Cl})	176.1(4) - 179.0(4)	1.957(8) - 1.965(8)	1.986(8) - 2.000(8)	1.099(12) - 1.114(14)
3	**5d** (IPr*)	176.6(2)	1.963(4)	2.016(5)	1.080(11)

[a]Two molecules were found in the crystal lattice of this complexes: the range of distances and angles obtained is given.

CONCLUSIONS

We have shown that the use of a solution of potassium *tert*-amylate in toluene leads to the rapid synthesis of [Au(OH)(NHC)] (**2**) from [AuCl(NHC)] (**1**) and from [AuCl(DMS)] and NHC·HCl salts. Expansion of this methodology has permitted the synthesis of [Au(NHC)(CH$_2$COCH$_3$] (**3**) from the same starting materials by simply exchanging the solvent. These gold acetonyl complexes have been shown as excellent replacements for gold hydroxides and can be used as precursors for the synthesis of [Au(NTf$_2$)(NHC)] (**4**) and [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**). Combination of these steps has permitted the sequential syntheses of a range of cationic complexes directly from the various chloride precursors. The possibility to tune the solvent used in the first reaction step of these procedures to ensure the formation of a stable intermediate (*i.e.* an acetonyl complex instead of a hydroxide complex) holds significant potential. By employing these strategies, known [Au(NTf$_2$)(IMes)] (**4e**) and [Au(NTf$_2$)(IAd)] (**4g**) are now available in a silver-free fashion and the range of [Au(NHC)(NCCH$_3$)][BF$_4$] (**5**) has been expanded to those bearing SIPr, IPr^{Cl}, IPr* and IAd ligands. Further investigations on the properties and applications of these complexes are currently ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information on reagents and characterization data for known compounds can be found in the Supporting Information. Yields for syntheses according to the various procedures are listed in Tables 1-4.

Procedure IVC for synthesis of [Au(OH)(NHC)] (2). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 1.5 equiv.) was added to a stirred solution of [AuCl(NHC)] (**1**) (1 equiv.) in toluene (0.1 mol L^{-1}). The reaction was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Water (excess, about the same value as base used) was added to the filtrate and it was concentrated. The product was precipitated by addition of pentane (about the initial reaction volume), collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure IVD for synthesis of [Au(OH)(NHC)] (2). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 1.5 equiv.) was added to a stirred solution of [AuCl(DMS)] (**1**) (1 equiv.) and NHC·HCl (1 equiv.) in THF/toluene (1:1, 0.1 mol L^{-1}). It was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Water (excess) was added to the filtrate and it was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VB for synthesis of [Au(CH$_2$COCH$_3$)(NHC)] (3). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 3.0 equiv.) was added to a stirred solution of [AuCl(NHC)] (**1**) (1 equiv.) in acetone (0.1 mol L^{-1}). It was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed from the filtrate under vacuum and the solid was dissolved in dichloromethane (about 0.5 mol L^{-1}) and filtered through silica with additional dichloromethane (about the initial reaction volume). The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VD for synthesis of [Au(CH$_2$COCH$_3$)(NHC)] (3). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 3.0 equiv.) was added to a stirred solution of [AuCl(DMS)] (1 equiv.) and NHC·HCl (1 equiv.) in toluene/acetone (1:1, 0.1 mol L^{-1}). It was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed from the filtrate under vacuum and the solid was dissolved in dichloromethane (about 0.5 mol L^{-1}) and filtered through silica with additional dichloromethane (about the initial reaction volume). The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIID for synthesis of [Au(NTf$_2$)(NHC)] (4). Bis(trifluoromethanesulfonyl)amine (1.1 equiv.) was added to a stirred solution of [Au(CH$_2$COCH$_3$)(NHC)] (**3**) (1 equiv.) in

dichloromethane (0.1 mol L^{-1}). After 10 minutes at rt, the solution was filtered through Celite® with additional dichloromethane (about the initial reaction volume). The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIIC for synthesis of [Au(NTf$_2$)(NHC)] (4). A solution of KO^{t}Am in toluene (1.7 mol L-1, 1.5 equiv.) was added to a stirred solution of [AuCl(NHC)] (**1**) (1 equiv.) in toluene (0.1 mol L^{-1}). It was stirred at room temperature for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed under vacuum, the solid was dissolved in dichloromethane (0.1 mol L^{-1}) and bis(trifluoromethanesulfonyl)amine (1.1 equiv.) was added to this stirred solution. After 10 minutes at rt, the solution was filtered through Celite® with additional dichloromethane (about the initial reaction volume). The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIIE for synthesis of [Au(NTf$_2$)(NHC)] (4). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 3.0 equiv.) was added to a stirred solution of [AuCl(DMS)] (**1**) (1 equiv.) and NHC·HCl (1 equiv.) in toluene/acetone (1:1, 0.1 mol L^{-1}). It was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed under vacuum, the solid was dissolved in dichloromethane (0.1 mol L^{-1}) and bis(trifluoromethanesulfonyl)amine (1.1 equiv.) was added to this stirred solution. After 10 minutes at rt, the solution was filtered through Celite®. The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIID' for synthesis of [Au(NHC)(NCCH$_3$)][BF$_4$] (5). Tetrafluoroboric acid diethyl ether complex (1.1 equiv.) was added to a stirred solution of [Au(CH_2COCH_3)(NHC)] (**3**) (1 equiv.) in acetonitrile (0.1 mol L^{-1}). After 10 minutes at rt, the solution was filtered through magnesium sulfate. The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIIC' for synthesis of [Au(NHC)(NCCH$_3$)][BF$_4$] (5). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 1.5 equiv.) was added to a stirred solution of [AuCl(NHC)] (**1**) (1 equiv.) in toluene (0.1 mol L^{-1}). It was stirred at room temperature for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed under vacuum, the solid was dissolved in dichloromethane (0.1 mol L^{-1}) and tetrafluoroboric acid diethyl ether complex (1.1 equiv.) was added to this stirred solution. After 10 minutes at rt, the solution was filtered through Celite®, concentrated, precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Procedure VIIE' for synthesis of [Au(NHC)(NCCH$_3$)][BF$_4$] (5). A solution of KO^{t}Am in toluene (1.7 mol L^{-1}, 3.0 equiv.) was added to a stirred solution of [AuCl(DMS)] (1 equiv.) and NHC·HCl (1 equiv.) in toluene/acetone (1:1, 0.1 mol L^{-1}). It was stirred at rt for 1 h and then filtered through Celite® with additional toluene (about twice the reaction volume). Solvent was removed under vacuum, the solid was dissolved in dichloromethane (0.1 mol L^{-1}) and tetrafluoroboric acid diethyl ether complex (1.1 equiv.) was added to this stirred solution. After 10 minutes at rt, the solution was filtered through Celite®. The solution was concentrated (to about 2 mol L^{-1}) and the product was precipitated by addition of pentane (about the initial reaction volume). It was collected by filtration, washed with additional pentane (about twice the initial reaction volume) and dried under high vacuum.

Characterization data.

[Au(SIPr)(NCCH$_3$)][BF$_4$] (**5b**). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; *p*-Ph*H*), 7.26 (d, $^3J_{H,H}$ =7.8 Hz, 4H; *m*-Ph*H*), 4.23 (s, 4H; CH_2), 2.98 (h, $^3J_{H,H}$ = 6.8 Hz, 4H; C*H*), 2.33 (s, 3H; CH_3), 1.34 (d, $^3J_{H,H}$ = 6.7 Hz, 12H; CH_3), 1.33 (d, $^3J_{H,H}$ = 6.5 Hz, 12H; CH_3). ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 188.3 (C_{carb}), 146.7 (*o*-Ph*C*), 133.2 (*i*-Ph*C*), 130.7 (*p*-Ph*C*), 124.9 (*m*-Ph*C*), 121.1 (*C*N), 54.2 (*C*H$_2$), 29.0 (*C*H), 25.5 (*C*H$_3$), 24.1 (*C*H$_3$), 2.7 (*C*H$_3$). ^{19}F{^{1}H}-NMR (377 MHz, $CDCl_3$): δ = -153.6. FTIR (ATR): ν = 2359-2303 cm^{-1} (C≡N).

[Au(IPr^{Cl})(NCCH$_3$)][BF$_4$] (**5c**). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.66 (t, $^3J_{H,H}$ = 7.8 Hz, 2H; *p*-Ph*H*), 7.40 (d, $^3J_{H,H}$ = 7.8 Hz, 4H; *m*-Ph*H*), 2.44 (s, 3H; CH_3), 2.32 (h, $^3J_{H,H}$ = 6.8 Hz, 4H; C*H*), 1.33–1.27 (m, 24H; CH_3). ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 166.4 (C_{carb}), 146.0 (*o*-Ph*C*), 132.7 (*p*-Ph*C*), 130.3 (*i*-Ph*C*), 125.2 (*m*-Ph*C*), 121.8 (*C*N), 120.6 (*C*), 29.4 (*C*H), 25.0 (*C*H$_3$), 23.6 (*C*H$_3$), 2.9 (*C*H$_3$). Anal. calcd for: $C_{29}H_{37}AuBCl_2F_4N_3$: C, 44.52; H, 4.77; N, 5.37. Found: C, 44.51; H, 4.86; N, 5.31. ^{19}F{^{1}H}-NMR (282 MHz, $CDCl_3$): δ = -153.2. FTIR (ATR): ν = 2359-2309 cm^{-1} (C≡N).

[Au(IPr)(NCCH$_3$)][BF$_4$]* (**5d**). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.28-7.18 (m, 32H; *o*-Ph*H*+*m*-Ph*H*), 6.88 (s, 4H; *m*-Ph*H*) 6.85-6.83 (m, 8H; *p*-Ph*H*), 6.04 (s, 2H; C*H*), 5.07 (s, 4H; C*H*), 2.62 (s, 3H; CH_3), 2.27 (s, 6H; CH_3), ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 166.7 (C_{carb}), 142.8 (Ph*C*), 141.6 (Ph*C*), 141.1 (*i*-Ph*C*), 140.6 (*i*-Ph*C*), 132.8 (*p*-Ph*C*), 130.8 (*p*-Ph*H*), 129.6 (*m*-Ph*C*), 129.4 (*m*-Ph*C*), 129.0 (*o*-Ph*C*), 128.8 (*o*-Ph*C*), 127.4 (*m*-Ph*C*), 127.3 (*m*-Ph*C*), 124.4 (*C*), 120.8 (*C*N), 51.5 (*C*H), 22.0 (*C*H$_3$), 2.9 (*C*H$_3$). ^{19}F{^{1}H}-NMR (377 MHz, $CDCl_3$): δ = -153.1. FTIR (ATR): ν = 2357-2308 cm−1 (C≡N).

[Au(IAd)(NCCH$_3$)][BF$_4$] (**5g**). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.26 (s, 2H; C*H*), 2.63 (s, 3H; CH_3), 2.45 (d, $^3J_{H,H}$ = 2.5 Hz, 12H; CH_2), 2.31 (br m, 6H; C*H*), 1.77 (q, $^3J_{H,H}$ = 12.0 Hz, 12H; CH_2). ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ = 156.9 (C_{carb}), 121.9 (*C*N), 117.3 (*C*H), 59.8 (*C*), 44.9 (*C*H), 35.8 (*C*H$_2$), 29.9 (*C*H$_2$), 3.2 (*C*H$_3$). ^{19}F{^{1}H}-NMR (471 MHz, $CDCl_3$): δ = -153.3. Anal. calcd for: $C_{25}H_{35}AuBF_4N_3$: C, 45.40; H, 5.33; N, 6.35. Found: C, 45.23; H, 5.49; N, 6.17.

ASSOCIATED CONTENT

Supporting Information

Text, schemes and tables giving general information on optimization studies, references for known complexes and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 1510730 (for **5b**), 1510731 (for **5c**), 1510732 (for **5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

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ABBREVIATIONS

DMS, dimethyl sulfide; IAd, 1,3-di(adamantyl)imidazol-2-ylidene; ICy, 1,3-bis(cyclododecyl)imidazol-2-ylidene; IDD, 1,3-bis(cyclododecyl)imidazol-2-ylidene; IMes, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; IPr, 1,3-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene; IPr^{Cl}, 4,5-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; IPr*, 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene; IPr^{*Tol}, 1,3-bis(2,6-bis(di-ptolylmethyl)-4-methylphenyl)imidazol-2-ylidene); I^tBu, 1,3-bis(tertbutyl)imidazol-2-ylidene. IPr^{Me}, 4,5-dimethyl-bis(2,6-di*iso*propylphenyl)imidazol-2-ylidene; nd, not determined; NHC, N-heterocyclic carbene; NMR, nuclear magnetic resonance; rt, room temperature; SIMes, 1,3-bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene; SIPr, 1,3-bis(2,6-di*iso*propylphenyl)imidazolin-2-ylidene.

REFERENCES

1. (a) Hashmi, A. S. K., *Gold Bull.* **2004,** *37*, 51-65; (b) Hashmi, A. S. K.; Hutchings, G. J., *Angew. Chem. Int. Ed.* **2006,** *45*, 7896-7936; (c) Hashmi, A. S. K., *Chem. Rev.* **2007,** *107*, 3180-3211; (d) Raubenheimer, H. G.; Cronje, S., *Chem. Soc. Rev.* **2008,** *37*, 1998-2011; (e) Arcadi, A., *Chem. Rev.* **2008,** *108*, 3266-3325; (f) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B., *Chem. Rev.* **2009,** *109*, 3561-3598; (g) Gagosz, F., *Tetrahedron* **2009,** *65*, 1757; (h) Raubenheimer, H. G.; Schmidbaur, H., *J. Chem. Educ.* **2014,** *91*, 2024-2036; (i) Wang, Y.-M.; Lackner, A. D.; Toste, F. D., *Acc. Chem. Res.* **2014,** *47*, 889-901; (j) Abbiati, G.; Rossi, E., *Beilstein J. Org. Chem.* **2014,** *10*, 481-513; (k) Pflästerer, D.; Hashmi, A. S. K., *Chem. Soc. Rev.* **2016,** *45*, 1331-1367.

2. (a) Herrmann, W. A., *Angew. Chem. Int. Ed.* **2002,** *41*, 1290-1309; (b) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics*, **2005**, *24*, 2411-2418; (c) Marion, N.; Nolan, S. P., *Chem. Soc. Rev.* **2008,** *37*, 1776-1782; (d) Gorin, D. J.; Sherry, B. D.; Toste, F. D., *Chem. Rev.* **2008,** *108*, 3351-3378; (e) Nolan, S. P., *Acc. Chem. Res.* **2011,** *44*, 91-100; (f) Gaillard, S.; Cazin, C. S. J.; Nolan, S. P., *Acc. Chem. Res.* **2011,** *45*, 778-787.

3. (a) Bond, G. C., *Gold Bull.* **1972,** *5*, 11-13; (b) Komiya, S.; Kochi, J. K., *J. Organomet. Chem.* **1977,** *135*, 65-72; (c) Preisenberger, M.; Schier, A.; Schmidbaur, H., *J. Chem. Soc., Dalton Trans.* **1999**, 1645-1650; (d) Hashmi, A. S. K.; Schuster, A. M.; Gaillard, S.; Cavallo, L.; Poater, A.; Nolan, S. P., *Organometallics* **2011**, *30*, 6328-6337.

4. de Frémont, P.; Stevens, E. D.; Fructos, M. R.; Mar Díaz-Requejo, M.; Pérez, P. J.; Nolan, S. P., *Chem. Commun.* **2006**, 2045-2047.

5. Ricard, L.; Gagosz, F., *Organometallics* **2007,** *26*, 4704-4707.

6. Lu, Z.; Han, J.; Hammond, G. B.; Xu, B., *Org. Lett.* **2015,** *17*, 4534-4537.

7. (a) Dang, T. T.; Boeck, F.; Hintermann, L., *J. Org. Chem.* **2011,** *76*, 9353-9361; (b) Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X., *J. Am. Chem. Soc.* **2012,** *134*, 9012-9019; (c) Barrio, P.; Kumar, M.; Lu, Z.; Han, J.; Xu, B.; Hammond, G. B., *Chem. Eur. J.* **2016**, 16410-16414; (d) Silver salts are also present in the early synthesis of one [AuCl(NHC)] complex via transmetallation using Ag-NHC: Schneider, S. K.; Herrmann, W. A.; Herdtweck, E., *Z. Anorg. Allg. Chem.* **2003**, *629*, 2363-2370.

8. Schmidbaur, H.; Schier, A., *Z. Naturforsch.* **2011,** *66b*, 329-350.

9. (a) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Commun.* **2010,** *46*, 2742-2744; (b) Ramón, R. S.; Gaillard, S.; Slawin, A. M. Z.; Porta, A.; D'Alfonso, A.; Zanoni, G.; Nolan, S. P., *Organometallics* **2010,** *29*, 3665-3668; (c) Gómez-Suárez, A.; Ramón, R. S.; Slawin, A. M. Z.; Nolan, S. P., *Dalton Trans.* **2012,** *41*, 5461-5463.

10. Nahra, F.; Patrick, S. R.; Bello, D.; Brill, M.; Obled, A.; Cordes, D. B.; Slawin, A. M. Z.; O'Hagan, D.; Nolan, S. P., *ChemCatChem* **2014,** *7*, 240-244.

11. Brill, M.; Nahra, F.; Gómez-Herrera, A.; Zinser, C.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P., *ChemCatChem* **2017,** *9*, 117-120.

12. Boogaerts, I. I. F.; Nolan, S. P., *J. Am. Chem. Soc.* **2010,** *132*, 8858-8859.

13. Gaillard, S.; Bosson, J.; Ramón, R. S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Eur. J.* **2010,** *16*, 13729-13740.

14. Ramón, R. S.; Gaillard, S.; Poater, A.; Cavallo, L.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Eur. J.* **2011,** *17*, 1238-1246.

15. (a) Gasperini, D.; Collado, A.; Goméz-Suárez, A.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Eur. J.* **2015,** *21*, 5403-5412; (b) A similar coumpound, phosphine-based $[Au(CH_2COCH_3)(PMes_3)]$, recently showed some interesting activities, see: Hashmi, A. S. K.; Schäfer, S.; Wölfle, M.; Diez Gil, C.; Fischer, P.; Laguna, A.; Blanco, M. C.; Gimeno, M. C., *Angew. Chem. Int. Ed.* **2007**, *46*, 6184-6187.

16. Gatto, M.; Belanzoni, P.; Belpassi, L.; Biasiolo, L.; Del Zotto, A.; Tarantelli, F.; Zuccaccia, D., *ACS Catal.* **2016**, 7363-7376.

17. Huang, J.; Nolan, S. P., *J. Am. Chem. Soc.* **1999,** *121*, 9889-9890.

18. Jafarpour, L.; Stevens, E. D.; Nolan, S. P., *J. Organomet. Chem.* **2000,** *606*, 49-54.

19. Collado, A.; Gómez-Suárez, A.; Martin, A. R.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Commun.* **2013,** *49*, 5541-5543.

20. Nahra, F.; Patrick, S. R.; Collado, A.; Nolan, S. P., *Polyhedron* **2014,** *84*, 59-62.

21. Patrick, S. R.; Gómez-Suárez, A.; Slawin, A. M. Z.; Nolan, S. P., *Organometallics* **2014,** *33*, 421-424.

22. See SI for details.

23. Collado, A.; Bohnenberger, J.; Oliva-Madrid, M.-J.; Nun, P.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P., *Eur. J. Inorg. Chem.* **2016**, 4111-4122.

24. Gaillard, S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P., *Organometallics* **2010,** *29*, 5402-5408.

25. Gómez-Suárez, A.; Ramón, R. S.; Songis, O.; Slawin, A. M. Z.; Cazin, C. S. J.; Nolan, S. P., *Organometallics* **2011,** *30*, 5463-5470.

26. Yields obtained were proportional to scale due to reduced mechanical losses during work-up.

27. Optimization studies of the solvent are described in the SI.

28. Because of the unsatisfactory results of complexes bearing the ICy ligand (Tables 2 and 3), these were excluded from further studies.

29. (a) Veenboer, R. M. P.; Dupuy, S.; Nolan, S. P., *ACS Catal.* **2015,** *5*, 1330-1334; (b) Veenboer, R. M. P.; Nolan, S. P., *Green Chem.* **2015,** *17*, 3819-3825.

30. Müller, R. S. R. Homogeneous gold catalysts: development of applications for gold(I) catalysts bearing *N*-heterocyclic carbene ligands. University of St Andrews, 2011.

31. (a) Herrmann, W. A.; Runte, O.; Artus, G., *J. Organomet. Chem.* **1995,** *501*, C1-C4; (b) de Frémont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P., *Organometallics* **2007,** *26*, 1376-1385; (c) Tapu, D.; Dixon, D. A.; Roe, C., *Chem. Rev.* **2009,** *109*, 3385-3407.

32. Upfield shifts are indicative of more Lewis acid gold centers.

33. Gaillard, S.; Bosson, J.; Ramón, R. S.; Nun, P.; Slawin, A. M. Z.; Nolan, S. P., *Chem. Eur. J.* **2010**, *16*, 13729−13740.

34. Chemical shifts for $[Au(NHC)][BF_4]$ (NHC = SIPr, IPr*) are still unknown. For synthesis and study of behavior of $[Au(IPr^{Cl})][BF_4]$, see: Veenboer, R. M. P.; Collado, A.; Dupuy, S.; Lebl, T.; Falivene, L.; Cavallo, L.; Cordes, D. B.; Slawin, A. M. Z.; Cazin, C. S. J.; Nolan S. P., *Organometallics* **2017**, *ASAP*; doi: 10.1021/acs.organomet.7b00345.

35. SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, September 14th, 2016)

36. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010,** *29*, 2176-2179.

37. Yau, J.; Michael P. Mingos, D., *J. Chem. Soc., Dalton Trans.* **1997**, 1103-1112.

38. Angell C. L.; Howell M. V., *J. Phys. Chem.* **1969**, *73*, 2551-2554.

39. (a) Back, O.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G., *Angew. Chem. Int. Ed.* **2013,** *52*, 2939-2943; (b) Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C., *Organometallics* **2013,** *32*, 5269-5272; (c) Nelson, D. J.; Nahra, F.; Patrick, S. R.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P., *Organometallics* **2014,** *33*, 3640-3645.

40. Brackemeyer, T.; Erker, G.; Fröhlich, R.; Prigge, J.; Peuchert, U., *Chem. Ber.* **1997**, *130*, 899-902.